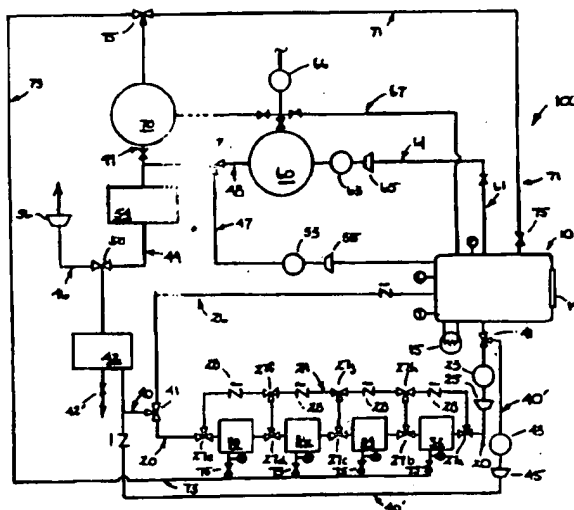




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : D06F 43/08		A1	(11) International Publication Number: WO 96/15304
			(43) International Publication Date: 23 May 1996 (23.05.96)
(21) International Application Number: PCT/US95/14643 (22) International Filing Date: 8 November 1995 (08.11.95) (30) Priority Data: 08/336,588 9 November 1994 (09.11.94) US 08/506,508 25 July 1995 (25.07.95) US (71) Applicant: R.R. STREET & CO. INC. [US/US]; 184 Shuman Boulevard, Naperville, IL 60563-8464 (US). (72) Inventor: STUCKER, John, F.; 27467 N. 75th Way, Scottsdale, AZ 85255 (US). (74) Agents: R. E. RT, Donald, W. et al.; Keck, Mahin & Cate, P.O. Box 10, Chicago, IL 60606-0110 (US).		(81) Designated States: AL, AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, R, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, LS, MW, SD, SZ, UG). Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	

(54) Title: METHOD AND SYSTEM FOR REJUVENATING PRESSURIZED FLUID SOLVENTS USED IN CLEANING SUBSTRATES



(57) Abstract

Method and system of rejuvenating pressurized fluid solvents used for cleaning a substrate in a pressurized vessel (10). A primary flow (20) of the pressurized fluid solvent is continuously cycled from the pressurized vessel through a series of filters (32-38) to remove insoluble and soluble contaminants, and then returned to the pressurized vessel (10). A secondary flow (40) of the pressurized fluid solvent, preferably equivalent to less than about 40 % of the primary flow, is directed to an evaporator (42) to evaporate the pressurized fluid solvent of the secondary flow into a vapor and to separate the contaminants therefrom. The vapor from the evaporator is then either liquified by a compressor or condenser (54) to create rejuvenated pressurized fluid solvent and redirected to the pressurized vessel for further use, or vented to atmosphere and replaced by new pressurized fluid solvent from a supply tank. Pressure equalization lines (71, 73) extend between a storage tank (70) and various system components to allow solvent vapor to displace therebetween.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

It is therefore advantageous to provide a method and system for cleaning substrates utilizing a solvent having less adverse consequence than those solvents typically used.

5 In this regard, the use of alternative pressurized liquid or dense fluid solvents has been suggested for cleaning various substrates, wherein dense fluids are widely understood to encompass gases that are pressurized to either subcritical or supercritical conditions so as to achieve a liquid or a supercritical fluid having a density approaching
10 that of a liquid. In particular, some patents have disclosed the use of a solvent such as carbon dioxide that is maintained in a liquid state or either a subcritical or supercritical condition for cleaning such substrates as clothing and precision metal parts.

15 As one example, expired U.S. Pat. 4,012,194 issued to Maffei discloses a garment cleaning process that uses liquid carbon dioxide. After passing through the garment, the liquid carbon dioxide solvent is circulated through an evaporator for removal of impurities, and then condensed by
20 a refrigerated storage unit before being returned for further use.

Later patents modify the Maffei approach. Particularly, U.S. Pat. 5,316,591, issued to Chao et al., is directed to a method of cleaning a substrate by cavitating a
25 liquified gas, such as liquid carbon dioxide. In the method disclosed by Chao et al., the substrate is placed in a cleaning chamber filled with the liquified gas, and a sonicating horn or similar cavitation-producing means is used to cavitate the liquified gas for a sufficient time to
30 remove undesired material from the substrate. In one embodiment of Chao et al., the liquified gas is simply purged after the cleaning process is complete. In another embodiment, a closed loop is specified, such that all of the liquified gas is recirculated after first being purified by
35 either vaporization, filtration, or an undefined combination of the two.

Rather than using liquified gas solvent, U.S. Pat. 5,013,366 issued to Jackson et al. is directed to a process

for removing two or more contaminants from a substrate using phase shifting of dense gases. Specifically, Jackson et al. disclose storing a substrate in a pressure vessel filled with a liquified gas, and then varying the temperature within the vessel to shift the liquified gas between a liquid state and a supercritical state. The contaminated liquified gas is then exhausted to a separator and recycled to the vessel for repeated use. However, the structure and operation of the separator are not described.

Also issued to Jackson et al., U.S. Pat. 5,213,619 discloses a process for cleaning and sterilizing a material using one or more dense fluids mixed with chemical agents, and simultaneously subjected to both a high energy source of acoustic radiation and a nonuniform electrostatic energy field. No solvent purification method appears to be disclosed.

U.S. Pat. 5,267,455 and PCT publication WO 94/01613 to Dewees et al. are directed to a dry cleaning system that uses supercritical carbon dioxide for cleaning clothing. Once cleaning is accomplished by agitation within a vessel, all of the supercritical carbon dioxide within the vessel is drained to a vaporizer vessel for removal of entrained contaminants and then condensed for reuse.

U.S. Pat. 5,279,615 issued to Mitchell et al., as well as related foreign patent applications by the same inventors, are also directed to a method of cleaning fabric using dense carbon dioxide. Mitchell et al. further require the use of a nonpolar cleaning adjunct, however, to clean the fabric. After cleaning, the dense carbon dioxide is simply directed to an expansion vessel so that the extracted soils can be collected, while the carbon dioxide is apparently vented.

U.S. Pat. 5,313,965 issued to Palen is directed to a continuous cleaning system using a supercritical fluid. The system disclosed by Palen includes a main processing vessel having an entry airlock and an exit airlock. In this manner, purging of the supercritical fluid and decompression of the main processing vessel are not required. Although

Palen states that the contaminated supercritical fluid may be processed in a conventional separator or recovery unit, no description of such separator or unit is provided.

5 Other patent publications that disclose cleaning processes using dense fluids include German patent application DE 3,904,514 and German patent DE 4,004,111. Both foreign publications disclose, among other things, purification by vaporization of all of the contaminated dense fluid prior to reuse.

10 As evident from the related art, conventional cleaning methods often require that the substrate to be cleaned is held within a bath of pressurized liquid or dense fluid solvent for a specific duration. This method may lead to recontamination of the substrate and degradation of efficiency since the contaminated solvent is not
15 continuously purified or removed from the system.

Additionally, after cleaning is complete, conventional methods typically either vent all of the contaminated solvent to atmosphere or recycle 100% of the contaminated
20 solvent for reuse after purification, such as by filtering or sequentially evaporating and condensing all of the solvent. It is believed, however, that efficiency is further degraded in each of these conventional cleaning methods. This is because it is costly to constantly replace
25 or evaporate and condense all of the solvent that is used. The conventional methods of venting or evaporating and condensing all of the solvent also result in a complete loss of all co-solvents and additives that are used in the cleaning process, which further increases costs. With
30 regard to the use of filtration alone, it is well known that this process allows soluble impurities to pass through the system and recontaminate the substrate.

There thus remains a need for an efficient and economic method and system for continuously rejuvenating pressurized
35 liquid or dense fluid solvents that are used for cleaning fabrics, delicate electronic components, and similar sensitive substrates, without adversely impacting the environment or wasting expensive co-solvents and additives.

DISCLOSURE OF THE INVENTION

The purpose and advantages of the present invention will be set forth in and apparent from the description that follows, as well as will be learned by practice of the invention. Additional advantages of the invention will be realized and attained by the methods and systems particularly pointed out in the written description and claims hereof, as well as from the appended drawings.

To achieve these and other advantages and in accordance with the purpose of the invention, as embodied and broadly described, the invention includes a method of continuously rejuvenating a pressurized liquid or dense fluid solvent used in cleaning a substrate, wherein the solvent is contaminated after contacting the substrate within a pressurized vessel. The term "dense fluid" is widely understood to refer to a gas or gas mixture that is compressed to either subcritical or supercritical conditions so as to achieve a liquid or a supercritical fluid having a density approaching that of a liquid. Hereinafter, the term "pressurized fluid solvent" will refer to both pressurized liquid and dense fluid solvents. Preferably, the pressurized fluid solvent used by the present invention is an inorganic substance, particularly carbon dioxide.

The method of the present invention includes the step of cycling a primary flow of the pressurized fluid solvent from the pressurized vessel through at least one filter to remove contaminants from the pressurized fluid solvent in the primary flow, and then cycling the primary flow back to the pressurized vessel after passing through the filter. Preferably, the primary flow of pressurized fluid solvent is cycled through a prefilter and a first filter to remove insoluble contaminants, as well as through an adsorption filter to remove soluble contaminants.

In addition to and in combination with the cycling step, a relatively small secondary flow, which may be either uniform or variable in rate, of the pressurized fluid solvent is directed from the pressurized vessel to an evaporator to evaporate the pressurized fluid solvent of the

secondary flow into a vapor and separate substantially all of the contaminants therefrom. Preferably, the pressurized fluid solvent is evaporated by altering the temperature within the evaporator, although it also may be necessary to vary the pressure within the evaporator particularly if the pressurized fluid solvent is at either the subcritical or supercritical condition prior to evaporation.

The secondary flow may be obtained directly from the pressurized vessel in one aspect of the invention, or the secondary flow may be obtained from a portion of the primary flow either before or after passing through the filter in another aspect of the invention. The volume of the secondary flow, which may be varied depending upon the needs of the cleaning process, is small relative to the total volume of pressurized fluid solvent in the pressurized vessel and primary flow line so as to reduce costs and conserve materials. This is generally accomplished by maintaining the secondary flow of pressurized fluid solvent equivalent to less than 40% of the primary flow, although a range between 2% and 25% is preferred and a range between 5% and 20% is even more preferred.

In one embodiment of the invention, the vapor from the evaporator is liquified to create purified pressurized fluid solvent substantially free of contaminants, and then redirected to the pressurized vessel for further use. Particularly, the vapor is liquified to either the liquid state or to either subcritical or supercritical conditions by altering the temperature, and possibly the pressure, of the vapor as necessary. The vapor also may be liquified by altering the pressure alone. Alternatively, and in accordance with another embodiment of the invention, the vapor is vented to an outside location and new pressurized fluid solvent is replaced into the pressurized vessel at a flow substantially equivalent to the amount vented. The separate steps of venting and liquifying the vapor from the evaporator also may be performed simultaneously in another embodiment of the invention.

The invention also includes a system for performing the various steps of the method summarized above and described in detail below. Various elements of the system include, among other things, a pressurized vessel for containing the substrate to be cleaned and a volume of the pressurized fluid solvent; a primary flow line for cycling a primary flow of the pressurized fluid solvent therethrough; at least one filter positioned along the primary flow line to remove contaminants from the pressurized fluid solvent of the primary flow; and a secondary flow line having an evaporator to evaporate a secondary flow of the pressurized fluid solvent into a vapor and separate contaminants therefrom. The secondary flow line may be in fluid communication with the pressurized vessel either directly by extending from the pressurized vessel, or indirectly by extending from the primary flow line at a location either before or after the filter.

Additionally, the system of the invention includes either a compressor or a condenser to liquify the vapor from the evaporator so as to create rejuvenated pressurized fluid solvent for further use in the pressurized vessel, or a vent to selectively vent the vapor from the evaporator to a location outside the system. In the preferred embodiment of the invention, the system is provided with both a condenser and a vent connected in parallel. Rather than providing the condenser as a separate component, however, the evaporator and condenser may be provided as an integral unit, preferably including a heat exchanger and pressure regulator for both evaporating and liquifying the pressurized fluid solvent. In this manner, separate outlets would be provided for venting the vapor or discharging the rejuvenated pressurized fluid solvent, respectively.

A source of new pressurized fluid solvent is also provided for initially charging the pressurized vessel, as well as for replacing new pressurized fluid solvent into the pressurized vessel at a flow substantially equivalent to the flow of pressurized fluid solvent that is removed by the secondary flow line and vented. This source may include

supply tank of fresh pressurized fluid solvent, or a storage tank of rejuvenated pressurized fluid solvent, or a combination of the two. Additionally, pressure equalization lines are provided between the storage tank and various system components to prevent the need for bleeding and cooling when these various system components are drained. The pressure equalization lines allow solvent vapor from the storage tank to replace pressurized fluid solvent that is drained from the system components, and conversely, allow the solvent vapor from the system components to cycle back to the storage tank when these system components are refilled with pressurized fluid solvent.

It is to be understood that both the foregoing general description and the following detailed description are exemplary and are intended to provide further explanation of the invention claimed.

The accompanying drawing, which is incorporated in and constitutes part of this specification, is included to illustrate and provide a further understanding of the method and system of the invention. Together with the description, the drawing serves to explain the principles of the invention.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a schematic representation of the system for cleaning a substrate in accordance with the invention.

BEST MODE FOR CARRYING OUT THE INVENTION

Reference will now be made in detail to the present preferred embodiments of the invention, an example of which is illustrated in the accompanying drawing. The steps of each method for cleaning the substrate and rejuvenating the pressurized fluid solvent that is used will be described in conjunction with the detailed description of the system.

The methods and systems presented herein may be used for cleaning a variety of substrates. The present invention is particularly suited for cleaning substrates such as fabrics, electronic components, and other flexible,

delicate, or porous structures that are sensitive to soluble and insoluble contaminants. Of course, other more durable substrates may also be cleaned by the present invention. For purpose of explanation and illustration, and not
5 limitation, an exemplary embodiment of a system for cleaning such substrates in accordance with the invention is shown in Fig. 1 and is designated generally by reference character 100.

As shown in Fig. 1, the system 100 generally comprises
10 a pressurized vessel 10, a primary flow line 20 including one or more filters, and a secondary flow line 40 including an evaporator 42. The term "line" used herein is understood to refer to a piping network or similar conduit capable of being pressurized and conveying a fluid. Downstream of the
15 evaporator 42, a condenser 54 or a vent 56 or a combination of the two is provided. For purpose of illustration and clarity, the system shown in Fig. 1 includes both the condenser 54 and the vent 56, connected in parallel by a valve 50 for selective operation of each. Alternatively,
20 the evaporator 42 and the condenser 54 may be provided as an integral unit capable of both evaporating and liquifying the pressurized fluid solvent. In this manner, the integral unit would be positioned at the location of the valve 50, as shown in Fig. 1, and include one outlet directed to the vent
25 56 and another outlet directed toward return line 47.

The system 100 also includes a supply tank 60 of pressurized fluid solvent for initially charging the system 100, and for replacing pressurized fluid solvent into the
30 pressurized vessel 10 that is removed during operation, as will be described in greater detail below. A storage tank 70 is also provided to receive rejuvenated pressurized fluid solvent from the condenser 54 during operation, as well as to receive pressurized fluid drained from the pressurized
35 vessel 10 when necessary. Pressure equalization lines 71 and 73 extend from the storage tank 70 to the pressurized vessel 10 and to the filters along the primary flow line 20, respectively.

The solvent that is provided by the supply tank 60 and used for cleaning the substrate preferably is a pressurized liquid or dense fluid. As noted above, the term "dense fluid" is widely understood to refer to a gas or gas mixture that is maintained at either subcritical or supercritical conditions so as to achieve a liquid or a supercritical fluid having a density approaching that of a liquid. As further noted above, the term "pressurized fluid solvent" is used herein to refer to either pressurized liquid or dense fluid solvents. Although a variety of solvents may be used, it is preferred that an inorganic substance such as carbon dioxide, helium, argon, or nitrous oxide is selected for use as the pressurized fluid solvent. For cost and environmental reasons, liquid, supercritical, or subcritical carbon dioxide is selected in the preferred embodiment of the invention. The selected pressurized fluid solvent also must be compatible with the substrate being cleaned.

To maintain the solvent in the appropriate fluid state, the internal temperature and pressure of the system must be appropriately controlled relative to the critical temperature and pressure of the solvent. For example, the critical temperature and pressure of carbon dioxide is 32 degrees Celsius and 72.9 atmospheres, respectively. This may be performed in a conventional manner, such as by using a heat exchanger 15 in combination with a thermocouple T or similar register to control temperature. Likewise, pressurization of the system 100 may be performed using a pressure regulator 65 to regulate the pressure inherently provided by the supply tank 60, as well as by providing a pump 63 in combination with a pressure gauge P. The locations and number of thermocouples T and pressure gauges P shown in Fig. 1, as well as the locations and number of valves to be described below, are provided merely for the purpose of illustration and not limitation.

The system temperature and pressure may be monitored and controlled either manually, or by a conventional automated controller (not shown) that receives signals from the thermocouple T and pressure gauge P, and then sends

corresponding signals to the heat exchanger 15 and pump 63, respectively. Unless otherwise noted, the temperature and pressure is appropriately maintained throughout the system 100 during operation. As such, elements contained within the system 100 are constructed of sufficient size and material to withstand the temperature, pressure, and flow parameters required for operation, and may be selected from any of a variety of conventional hardware that is available.

As well as charging or filling the system with the pressurized fluid solvent, additional co-solvents, detergents, or other conventional additives may be combined with the pressurized fluid solvent to enhance the cleaning capability of the system 100. These additives may be premixed with the pressurized fluid solvent in the supply tank 60, or as shown in Fig. 1, they may be injected intermittently or continuously by a pump 66 through injection lines 67 into the tanks 60 and 70 or the pressurized vessel 10. Hereinafter, the term "pressurized fluid solvent" will be further understood as inclusive of any additives that may have been provided.

The substrate to be cleaned is placed within the pressurized vessel 10 through vessel door 19. This may be performed prior to charging or filling the system 100 with the pressurized fluid solvent. Preferably, however, valves are provided to purge and seal off the pressurized vessel 10 so that the substrate may be loaded and unloaded without depressurizing the remainder of the system 100. Alternatively, the pressurized vessel 10 may include an entry airlock (not shown) to allow loading and unloading of substrates without purging the pressurized vessel 10. In any event, the pressurized vessel should be configured and constructed to withstand operating pressures between about 5.5 and about 10.5 MPa (i.e., from about 800 psig to about 1500 psig).

To clean the substrate, the pressurized vessel 10 is filled with the pressurized fluid solvent from either the supply tank 60 or the storage tank 70. The pressurized fluid solvent is maintained at an appropriate level in the

pressurized vessel 10 throughout the cleaning operation by a level controller L. The level controller L sends a signal to the controller (not shown), which controls pump 63 and regulator 65 to regulate the outflow of solvent from the supply tank 60. Alternatively, or in addition to using the supply tank 60, rejuvenated pressurized fluid may be provided from storage tank 70 by pump 53 and regulator 55 through return line 47. If pumps 53 and 63 are reversible, then lines 47 and 61 may be used for purging or draining the pressurized vessel 10 as well. A direct line (not shown) between the storage tank 70 and pressurized vessel 10 also may be provided if desired.

Once the pressurized fluid solvent contacts the substrate within the pressurized vessel 10, contaminants from the substrate become entrained in and contaminate the solvent. As such, and in accordance with the present invention, the pressurized fluid solvent is continuously rejuvenated to remove soluble and insoluble contaminants and prevent recontamination of the substrate. This is performed efficiently and effectively by a novel combination of filtration, adsorption, and evaporation, as will be described.

Specifically, and in accordance with the present invention, a primary flow of the pressurized fluid solvent is cycled from the pressurized vessel through at least one filter to remove contaminants from the pressurized fluid solvent in the primary flow. As shown in Fig. 1 and embodied herein, a conventional pump 23 and regulator 25 are provided to cycle the primary flow of pressurized fluid solvent through a primary line 20. The required flow rate of the primary flow will vary depending upon the total volume of the system and the quantity and type of insoluble contaminants present. The filtration process to be described is preferably performed continuously throughout the cleaning process to prevent recontamination of the substrate being cleaned in the pressurized vessel 10.

Although Fig. 1 shows a series of filters positioned along the primary flow line 20, it is possible that the use

of only one filter may be adequate to remove contaminants from the pressurized fluid solvent. In the preferred embodiment, however, the system includes a prefilter 32, a first filter 34, and an adsorption filter 36, and perhaps
5 even a polishing filter 38. The use of several filters connected in series, as shown in Fig. 1, enhances the transfer and removal of contaminants from the pressurized fluid solvent of the primary flow.

The prefilter 32 is provided for the removal of larger
10 insoluble contaminants that would likely degrade subsequent filtration. To accomplish this, the prefilter 32 preferably is constructed of woven nylon or other material not adversely affected by the solvent, co-solvent, and other additives, and has a mesh size of between about 50 and 100.

15 Positioned downstream of the prefilter 32 along the primary flow line 20 is a first filter 34 for the removal of additional insoluble contaminants that are entrained within the primary flow of pressurized fluid solvent. This filter 34 preferably has a particle retention capability of between
20 about 5 and 50 microns, depending upon the requirements of the system 10. A cartridge filter having a suitable septum, such as paper, polypropylene, glass, or similar non-woven substrate is preferred for filter 34, although a diatomaceous earth filter or a powderless filter with an
25 appropriate septum likewise may be used. If necessary or desired, additional filters of similar or finer mesh than that of first filter 34 may be provided downstream of filter 34 for enhanced filtration of insoluble contaminants. Alternatively, or additionally, a centrifuge may be provided
30 to separate insoluble particles from the pressurized fluid solvent. Such centrifuges are conventional and known in the art.

The preferred embodiment shown in Fig. 1 also includes an adsorptive filter 36 positioned downstream of the first
35 filter 34, as noted above. The adsorptive filter 36 is used for the control and removal of undesirable soluble contaminants, such as fugitive dyes obtained from clothes or other substrates during the cleaning process. Generally,

adsorbents that may be used include activated carbon, clay, or a combination of the two. Alternative adsorbents likewise are widely known, and may be selected to satisfy the specific soluble contaminants expected to be encountered.

A polishing filter 38 also may be positioned along the primary flow line 20 if desired, or if required due to the sensitive nature of the substrate. The polishing filter 38 is provided for the removal of any fine insoluble contaminants that either bypass or are not filtered by the prefilter 32 and first filter 34, as well as for the removal of any adsorbents that may be released inadvertently by the adsorptive filter 36. The preferred construction of the polishing filter 38 is a string wound filter or microporous cartridge filter having a particle retention capability of about 1 micron.

For enhanced versatility, the preferred embodiment of the system also includes bypass line 24 connected by bypass valves 27a-27e for selectively or automatically bypassing one or more of the filters when desired or when extensive filtration is deemed unnecessary. Check valves 28 are provided to ensure that flow is not reversed through the bypass line 24. Fig. 1 shows, for purpose of illustration and not limitation, that each one or any combination of the filters may be bypassed selectively by proper operation of bypass valves 27a-27e. For example, if adsorption is not desired, filter 36 effectively can be removed from the system 100 by operation of the bypass valves 27c, 27g, 27f, and 27d. The primary flow would therefore be cycled from valve 27a through elements 32, 27b, 34, 27c, 27g, 27f, 27d, 38, and 27e, in order. Alternative bypass configurations likewise may be used.

After passing through the filters, the primary flow of pressurized fluid solvent is cycled back to the pressurized vessel 10 through return line 26. Filtration along the primary flow line should therefore be established, by selecting the proper filters, so as to reduce the quantity of contaminants in the pressurized fluid solvent to a level

sufficient to preclude redeposition of contaminants onto the substrate when the pressurized fluid solvent is reintroduced into pressurized vessel 10 via return line 26. Although not shown, an auxiliary line also may be provided to direct the filtered pressurized fluid solvent to the storage tank 70. In this manner, the primary flow would be cycled back to the pressurized vessel 10 via the storage tank 70.

Further in accordance with the present invention, the methods and systems for rejuvenating pressurized fluid solvent include directing a secondary flow of the pressurized fluid solvent from the pressurized vessel to an evaporator to evaporate the pressurized fluid solvent of the secondary flow into a vapor and separate contaminants therefrom. The secondary flow may be either uniform or variable in rate during operation as will be described. Any soluble or insoluble contaminants entrained in the pressurized fluid solvent of the secondary flow are thus separated as a residue, which is easily collected in a conventional manner. Evaporation therefore further aids in maintaining the quantity of contaminants in the pressurized fluid solvent within an acceptable level.

The volume of pressurized fluid solvent directed to the secondary flow is small, and varied depending upon need, relative to the total volume of pressurized fluid solvent contained within the pressurized vessel and the primary flow line, including filters 32, 34, 36, and 38. In this manner, the costs associated with evaporation, and subsequent venting or liquification as will be described, are maintained low. Further, materials such as pressurized fluid solvent, co-solvents, and other additives used during the cleaning process are conserved to reduce costs and adverse environment effects. To ensure that only a relatively small volume of pressurized fluid solvent is evaporated, the secondary flow that is directed to the evaporator is maintained equivalent to less than about 40% of the primary flow, although a range of between about 2% and 25% is preferred, and a range of between about 5% and 20% is even more preferred. This flow may be maintained

uniform throughout operation for continuous rejuvenation, or may be variable in either an intermittent or a continuous manner if desired.

5 The system 100 embodied herein is provided with a secondary flow line in fluid communication with the pressurized vessel 10 to direct the secondary flow of pressurized fluid solvent to the evaporator 42. The secondary flow line preferably is connected to the primary
10 the filter or filters by a splitter valve 41 so as to reduce the number of required penetrations through the wall of the pressurized vessel 10. Alternatively, the secondary flow line may be connected directly to the pressurized vessel 10 if desired.

15 In the preferred embodiment of the invention, Fig. 1 shows that a secondary flow line 40 is connected downstream of the filters, and an additional secondary flow line 40' is connected upstream for greater versatility. Thus, filtered solvent may be obtained for evaporation through secondary
20 flow line 40, while unfiltered solvent may be obtained through secondary flow line 40'. The secondary flow may be either uniform or variable in rate, depending upon the amount of rejuvenation required, and is controlled by the splitter valves 41 in combination with the pumps and
25 regulators located along the secondary flow lines 40, 40'.

A variety of evaporator configurations and designs are available for use in the system of the present invention. For example, evaporation can be performed by adjusting the temperature within the evaporator 42, or by adjusting the
30 pressure within the evaporator 42, or by a combination of the two. The evaporator 42 therefore preferably includes a heat exchanger in combination with a pressure regulator to evaporate the pressured fluid solvent into a vapor or gas state, and thus separate substantially all of the
35 contaminants therefrom. For example, if the pressurized fluid solvent is initially a pressurized liquid, then evaporation may be performed by increasing the temperature within the evaporator while maintaining a constant pressure.

If the pressurized fluid solvent is a dense fluid in either the subcritical or supercritical conditions, then the pressure within the evaporator also will need to be adjusted to obtain the desired vapor or gas state while the temperature is adjusted accordingly.

The heat exchanger of the evaporator 42 may be a heat pump configuration, a combination of heating and cooling coils, or any other conventional temperature control device. Likewise, the pressure regulator of the evaporator may be a conventional pressure control valve, although the preferred embodiment also includes a compressor pump for increasing pressure within the evaporator as necessary. A thermocouple and pressure gauge also are provided for monitoring the operation of the evaporator 42. Additionally, a waste discharge line 42' or similar means is provided for removing the contaminants that are separated from the solvent after evaporation occurs. Evaporators including these features are conventional in design, and generally available so as to withstand the expected pressures and temperatures related with the system 100. Operation of the evaporator 42 may be controlled manually, or by a conventional automated controller (not shown) that receives signals from the thermocouple and pressure gauge.

Once the pressurized fluid solvent is evaporated, several options are available. In accordance with one embodiment of the invention, a condenser 54 is provided to liquify the vapor from the evaporator 42 and create rejuvenated pressurized fluid solvent substantially free of contaminants. The term "liquify" as used herein refers to altering a vapor from a gaseous state to a liquid state or to either a subcritical or a supercritical condition. This is performed by returning the temperature and pressure parameters within the condenser to the same or similar operating parameters of the remainder of the system 100. As with the evaporator 42, the condenser 54 embodied herein therefore includes a heat exchanger and a pressure regulator to adjust temperature and pressure, respectively, as well as a thermocouple and pressure gauge to monitor and control

operation. Such condensers are conventional in design and available to withstand the expected operating parameters of the system 100.

By locating the condenser 54 downstream from the evaporator 42, the pressurized fluid solvent may be rejuvenated in a continuous manner to remove soluble and insoluble contaminants and prevent recontaminating the substrate. In particular, and as shown in the embodiment of Fig. 1, the rejuvenated pressurized fluid solvent from the condenser 54 is directed through a return line 47 via pump 53 and regulator 55, if necessary, to the pressurized vessel 10 for further use. Alternatively, the rejuvenated solvent from the condenser 54 may be directed through auxiliary line 48 to the supply tank 60 or through auxiliary line 49 to the storage tank 70 for future use if desired.

Rather than using a condenser, it likewise is possible to use a compressor to liquify the vapor from the evaporator 42. Acceptable compressors are available from Blackmer Pump of Grand Rapids, Michigan, or Haskel International, Inc. of Burbank, California. These specific compressor model is based, however, on the capacity of the evaporator 42 and the demands of the system 100.

In accordance with another embodiment of the invention, the vapor from the evaporator may be vented to a location outside the system. This is accomplished by directing the vapor through a vent line 46 to a conventional vent 56 that is open to atmosphere. If the pressurized fluid solvent selected is carbon dioxide, then venting may be preferred due to its low cost and nontoxicity. For continuous operation of the system 100, however, a source of new pressurized fluid solvent is provided in fluid communication with the pressurized vessel 10 to replace new pressurized fluid solvent into the pressurized vessel 10 at a flow substantially equivalent to that of the secondary flow which is vented. Fig. 1 shows that the source of this new pressurized fluid solvent may be either the supply tank 60 or the storage tank 70. The flow of this pressurized fluid solvent from the supply tank 60 is regulated by the pump 63

and regulator 65 along the supply line 61, while the flow from the storage tank 70 is regulated by the pump 53 and regulator 55 along return line 47. As will be appreciated, the flow of the new pressurized fluid solvent may be maintained uniform throughout operation, or may be variable in either an intermittent or continuous manner.

Preferably, and according to another aspect of the invention, the system 100 is provided with both the condenser 54 and the vent 56, which are connected in parallel by valve 50. If valve 50 is a directional valve, then either the condenser 54 or the vent 56 may be selectively operated for rejuvenation of the pressurized fluid solvent. If a splitter valve is provided as the valve 50, however, then a portion of the vapor from the evaporator may be directed to the condenser 54 to create rejuvenated pressurized fluid solvent, while any remaining portion of the vapor is vented by the vent and replaced with new pressurized fluid solvent from either the supply tank 60 or the storage tank 70.

Rather than providing the evaporator 42 and the condenser 54 separately, and in accordance with yet another aspect of the invention, these two system components may be provided as an integral unit. This integral unit (not shown) would include a heat exchanger and pressure regulator for both evaporating and liquifying the pressurized fluid solvent as described above with regard to the separate components 42 and 54, as well as a thermocouple and pressure gauge to monitor and control operation. Rejuvenation of the pressurized fluid solvent by the integral unit therefore would be performed in a batch-type operation, wherein a batch of pressurized fluid solvent from the secondary flow is first evaporated and then liquified to create rejuvenated pressurized fluid solvent. The use of an integral unit is advantageous because redundant components would be eliminated, and thus, the cost of initial investment for the system would be reduced. Such integral units are conventional, or may be custom made to satisfy the system requirements.

If an integral unit is provided in lieu of a separate evaporator 42 and condenser 54, then the integral unit would be positioned at the location of the valve 50 shown in Fig. 1. The integral unit would include one outlet directed to the vent 56 and another outlet directed toward the return line 47, each outlet including a valve to control flow in accordance with the operation the integral unit. Particularly, if liquification is performed to create rejuvenated pressurized fluid solvent substantially free of contaminants, then the outlet directed toward the return line 47 would be opened to discharge the rejuvenated pressurized fluid solvent to either the storage tank 70 or the pressurized vessel 10. Alternatively, if venting is preferred, then the outlet directed toward the return line 47 would be closed and the outlet directed to the vent 56 would be opened once evaporation occurred.

During operation of the system 100, it may be necessary to remove or drain pressurized fluid solvent from various system components, such as the pressurized vessel 10 and the filters 32, 34, 36 and 38. Rather than venting this drained pressurized fluid solvent to atmosphere, it is preferred that the drained pressurized fluid solvent from the desired system component is directed to the storage vessel 70 for subsequent reuse. Pressure equalization lines 71 and 73 therefore are provided to prevent compression, and thus excessive heating, of the solvent vapor that is contained within the storage tank 70 as the drained pressurized fluid solvent is introduced into the storage tank 70.

Particularly, as new pressurized fluid solvent is introduced into the storage tank 70, solvent vapor is displaced through the appropriate pressure equalization line 71 and 73 to the system component that is being drained. Valves 75 are provided along the pressure equalization lines 71 and 73 to direct the solvent vapor accordingly. Conversely, when the drained system component is refilled with pressurized fluid solvent from the storage tank 70, the solvent vapor is then displaced and returned through the corresponding pressure equalization line 71 and 73 to the

storage tank 70. Sight glasses or level sensors S are provided to indicate when filling is complete.

Additionally, pumps (not shown) may be provided along the pressure equalization lines 71 and 73, such that solvent vapor is actively drawn from the storage tank 70 to purge pressurized fluid solvent from the system component to be drained. Although not shown, similar pressure equalization lines may be provided between the supply tank 60 and the various system components to be drained.

The methods and systems of the present invention, as described above and shown in Fig. 1, provide for continuous filtration of a primary flow of contaminated pressurized fluid solvent to remove insoluble and soluble contaminants, and for continuous evaporation of a secondary flow to enhance rejuvenation. Additionally, the system includes pressure equalization lines to prevent compression of solvent vapors, and therefore, eliminates the need for system bleeding or cooling. The present invention thus provides for the conservation of the pressurized fluid solvent, co-solvents and other additives used, as well as for the conservation of energy and time typically expended in conventional cleaning methods. Likewise, evaporator and condenser size requirements are reduced by the present invention, thereby reducing both operating and equipment costs of the system.

It will be apparent to those skilled in the art that various modifications and variations can be made in the method and system of the present invention without departing from the spirit or scope of the invention. Thus, it is intended that the present invention cover modifications and variations that come within the scope of the appended claims and their equivalents.

CLAIMS

What Is Claimed Is:

1. A method of rejuvenating a pressurized fluid solvent used for cleaning a substrate, the pressurized fluid solvent being contaminated with contaminants after cleaning the substrate within a pressurized vessel, the method
5 comprising the steps of:
cycling a primary flow of the pressurized fluid solvent from the pressurized vessel through at least one filter to remove contaminants from the pressurized fluid solvent in the primary flow, the primary flow being cycled
10 back to the pressurized vessel after passing through the filter;
directing a secondary flow of the pressurized fluid solvent from the pressurized vessel to an evaporator to evaporate the pressurized fluid solvent of the secondary
15 flow into a vapor and to separate contaminants therefrom;
liquifying the vapor of the secondary flow from the evaporator to create rejuvenated pressurized fluid solvent substantially free of contaminants; and
redirecting the rejuvenated pressurized fluid
20 solvent of the secondary flow to the pressurized vessel for further use.
2. The method of claim 1, wherein the cycling step includes cycling the primary flow of pressurized fluid solvent through a first filter to remove insoluble contaminants and an adsorption filter to remove soluble
5 contaminants.
3. The method of claim 2, wherein the cycling step further includes cycling the primary flow of pressurized fluid solvent through a prefilter to remove insoluble contaminants prior to cycling the primary flow of
5 pressurized fluid solvent through the first filter and the adsorption filter.

4. The method of claim 1, wherein the cycling step is performed continuously while the substrate is being cleaned.

5. The method of claim 1, wherein the secondary flow of pressurized fluid solvent directed from the pressurized vessel by the directing step is equivalent to less than about 40% of the primary flow of pressurized fluid solvent
5 cycled by the cycling step.

6. The method of claim 5, wherein the secondary flow of pressurized fluid solvent is equivalent to between about 2% and 25% of the primary flow of pressurized fluid solvent.

7. The method of claim 1, wherein the secondary flow of pressurized fluid solvent directed from the pressurized vessel by the directing step is obtained from at least a portion of the primary flow of pressurized fluid solvent
5 after passing through the filter.

8. The method of claim 1 further including the steps of venting a portion of the vapor of the secondary flow from the evaporator to an outside location, and replacing new pressurized fluid solvent into the pressurized vessel at a
5 flow substantially equivalent to the portion of the secondary flow vented by the venting step; and further wherein the liquifying step includes liquifying any remaining vapor of the secondary flow from the evaporator not vented by the venting step.

9. The method of claim 1 further including the step of selecting as the pressurized fluid solvent an inorganic substance for cleaning the substrate.

10. The method of claim 1, wherein the directing step includes evaporating the pressurized fluid solvent of the secondary flow by adjusting the temperature of the pressurized fluid solvent.

11. The method of claim 10, wherein the liquifying step includes liquifying the vapor of the secondary flow by adjusting the temperature of the vapor.

12. The method of claim 1, wherein the directing step includes evaporating the pressurized fluid solvent of the secondary flow by adjusting the pressure of the pressurized fluid solvent.

13. The method of claim 12, wherein the liquifying step includes liquifying the vapor of the secondary flow by adjusting the pressure of the vapor.

14. The method of claim 1, wherein the liquifying step is performed continuously while the substrate is being cleaned.

15. The method of claim 1, wherein the liquifying step is performed in a batch-type manner while the substrate is being cleaned.

16. A method of rejuvenating a pressurized fluid solvent used for cleaning a substrate, the pressurized fluid solvent being contaminated with contaminants after cleaning the substrate within a pressurized vessel, the method comprising the steps of:

5 cycling a primary flow of the pressurized fluid solvent from the pressurized vessel through at least one filter to remove contaminants from the pressurized fluid solvent in the primary flow, the primary flow being cycled
10 back to the pressurized vessel after passing through the filter;

directing a secondary flow of the pressurized fluid solvent from the pressurized vessel to an evaporator to evaporate the pressurized fluid solvent of the secondary
15 flow into a vapor and to separate contaminants therefrom;

venting the vapor of the secondary flow from the evaporator to an outside location; and

replacing new pressurized fluid solvent into the
pressurized vessel at a flow substantially equivalent to the
20 secondary flow vented by the venting step.

17. The method of claim 16, wherein the cycling step
includes cycling the primary flow of pressurized fluid
solvent through a first filter to remove insoluble
contaminants and an adsorption filter to remove soluble
5 contaminants.

18. The method of claim 17, wherein the cycling step
further includes cycling the primary flow of pressurized
fluid solvent through a prefilter to remove insoluble
contaminants prior to cycling the primary flow of
5 pressurized fluid solvent through the first filter and the
adsorption filter.

19. The method of claim 16, wherein the cycling step
is performed continuously while the substrate is being
cleaned.

20. The method of claim 16, wherein the secondary flow
of pressurized fluid solvent directed from the pressurized
vessel by the directing step is equivalent to less than
about 40% of the primary flow of pressurized fluid solvent
5 cycled by the cycling step.

21. The method of claim 20, wherein the secondary flow
of pressurized fluid solvent is equivalent to between about
2% and 25% of the primary flow of pressurized fluid solvent.

22. The method of claim 16, wherein the secondary flow
of pressurized fluid solvent directed from the pressurized
vessel by the directing step is obtained from at least a
portion of the primary flow of pressurized fluid solvent
5 after passing through the filter.

23. The method of claim 16 further including the steps of liquifying a portion of the vapor of the secondary flow from the evaporator to create rejuvenated pressurized fluid solvent substantially free of contaminants, and redirecting the rejuvenated pressurized fluid solvent to the pressurized vessel for further use; and further wherein the venting step includes venting any remaining vapor of the secondary flow from the evaporator not liquified by the liquifying step.

24. The method of claim 16 further including the step of selecting as the pressurized fluid solvent an inorganic substance for cleaning the substrate.

25. The method of claim 16, wherein the directing step includes evaporating the pressurized fluid solvent of the secondary flow by adjusting the temperature of the pressurized fluid solvent.

26. The method of claim 16, wherein the directing step includes evaporating the pressurized fluid solvent of the secondary flow by adjusting the temperature and the pressure of the pressurized fluid solvent.

27. The method of claim 16 further including the steps of liquifying a portion of the vapor of the secondary flow from the evaporator to create rejuvenated pressurized fluid solvent substantially free of contaminants, and redirecting the rejuvenated pressurized fluid solvent to the pressurized vessel for further use; and further wherein the venting step includes venting any remaining vapor of the secondary flow from the evaporator not liquified by the liquifying step.

28. The method of claim 27, wherein the liquifying step includes liquifying the vapor of the secondary flow by adjusting the temperature of the vapor.

29. The method of claim 27, wherein the liquifying step includes liquifying the vapor of the secondary flow by adjusting the pressure of the vapor.

30. The method of claim 27, wherein the liquifying step is performed continuously while the substrate is being cleaned.

31. The method of claim 27, wherein the liquifying step is performed in a batch-type manner while the substrate is being cleaned.

32. A system for cleaning a substrate using a pressurized fluid solvent, the system comprising:

a pressurized vessel for containing the substrate to be cleaned and a volume of the pressurized fluid solvent;

5 a primary flow line in fluid communication with the pressurized vessel, the primary flow line including a pump for cycling a primary flow of the pressurized fluid solvent therethrough;

10 at least one filter positioned along the primary flow line to remove contaminants from the pressurized fluid solvent of the primary flow, the primary flow line configured to cycle the pressurized fluid solvent of the primary flow back to the pressurized vessel after passing through the filter;

15 a secondary flow line in fluid communication with the pressurized vessel, the secondary flow line including an evaporator to evaporate a secondary flow of the pressurized fluid solvent directed through the secondary flow line into a vapor and to separate contaminants therefrom; and

20 a compressor in fluid communication with the evaporator to compress the vapor from the evaporator to create rejuvenated pressurized fluid solvent substantially free of contaminants, the compressor also in fluid communication with the pressurized vessel to redirect the
25 rejuvenated pressurized fluid solvent to the pressurized vessel for further use.

33. The system of claim 32 further including a selectively-operated vent connected in fluid communication with the evaporator and in parallel with the compressor to selectively vent at least a portion of the vapor from the evaporator to a location outside the system.

34. The system of claim 32 further including a source of new pressurized fluid solvent in fluid communication with the pressurized vessel to replace new pressurized fluid solvent into the pressurized vessel at a flow substantially equivalent to the portion of secondary flow vented by the vent.

35. The system of claim 32, wherein the primary flow line includes a first filter to remove insoluble contaminants and an adsorption filter to remove soluble contaminants.

36. The system of claim 32, wherein the secondary flow line is in fluid communication with the pressurized vessel by extending from and in fluid communication with the primary flow line at a location after the filter so that the secondary flow of pressurized fluid solvent is obtained from at least a portion of the primary flow of pressurized fluid solvent after passing through the filter.

37. A system for cleaning a substrate using a pressurized fluid solvent, the system comprising:

a pressurized vessel for containing the substrate to be cleaned and a volume of the pressurized fluid solvent;

a primary flow line in fluid communication with the pressurized vessel, the primary flow line including a pump for cycling a primary flow of the pressurized fluid solvent therethrough;

at least one filter positioned along the primary flow line to remove contaminants from the pressurized fluid solvent of the primary flow, the primary flow line configured to cycle the pressurized fluid solvent of the

primary flow back to the pressurized vessel after passing through the filter;

15 a secondary flow line in fluid communication with the pressurized vessel, the secondary flow line including an evaporator to evaporate a secondary flow of the pressurized fluid solvent directed through the secondary flow line into a vapor and separate contaminants therefrom;

20 a vent connected in fluid communication with the evaporator to vent the vapor from the evaporator to a location outside the system; and

a source of new pressurized fluid solvent in fluid communication with the pressurized vessel to replace new
25 pressurized fluid solvent into the pressurized vessel at a flow substantially equivalent to the secondary flow vented by the vent.

38. A system for cleaning a substrate using a pressurized fluid solvent, the system comprising:

a pressurized vessel for containing the substrate to be cleaned and a volume of the pressurized fluid solvent;

5 a primary flow line in fluid communication with the pressurized vessel, the primary flow line including a pump for cycling a primary flow of the pressurized fluid solvent therethrough;

10 at least one filter positioned along the primary flow line to remove contaminants from the pressurized fluid solvent of the primary flow, the primary flow line configured to cycle the pressurized fluid solvent of the primary flow back to the pressurized vessel after passing through the filter;

15 a secondary flow line in fluid communication with the pressurized vessel, the secondary flow line including an evaporator to evaporate a secondary flow of the pressurized fluid solvent directed through the secondary flow line into a vapor and to separate contaminants therefrom; and

20 a condenser in fluid communication with the evaporator to liquify the vapor from the evaporator to create rejuvenated pressurized fluid solvent substantially

free of contaminants, the condenser also in fluid
communication with the pressurized vessel to redirect the
25 rejuvenated pressurized fluid solvent to the pressurized
vessel for further use.

39. The system of claim 38, wherein the evaporator and
the condenser each include a heat exchanger for adjusting
temperature and a pressure regulator for adjusting pressure.

40. The system of claim 39, wherein the evaporator and
the condenser are provided together as an integral unit.

41. The system of claim 38 further including a tank in
fluid communication with the pressurized vessel for storing
and supplying pressurized fluid solvent, and a pressure
equalization line in fluid communication with and extending
5 between the tank and at least one of either the filter and
the pressurized vessel for displacing solvent vapor
therebetween.

42. The system of claim 38 further including a
selectively-operated vent connected in fluid communication
with the evaporator and in parallel with the condenser to
selectively vent at least a portion of the vapor from the
5 evaporator to a location outside the system.

43. A system for cleaning a substrate using a
pressurized fluid solvent, the system comprising:

a pressurized vessel for containing the substrate
to be cleaned and a volume of the pressurized fluid solvent;

5 a primary flow line in fluid communication with
the pressurized vessel, the primary flow line including a
pump for cycling a primary flow of the pressurized fluid
solvent therethrough;

10 at least one filter positioned along the primary
flow line to remove contaminants from the pressurized fluid
solvent of the primary flow, the primary flow line
configured to cycle the pressurized fluid solvent of the

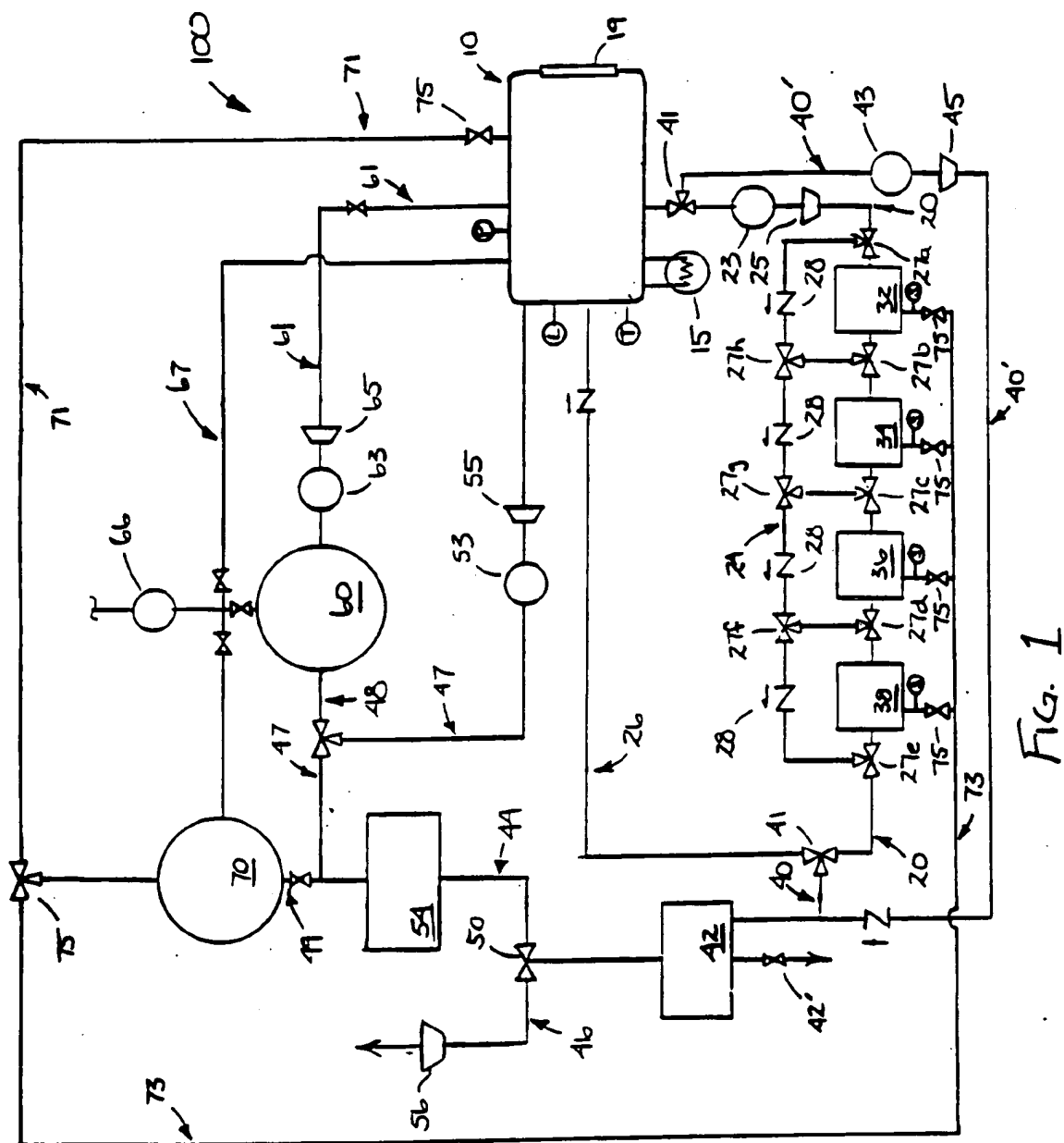
primary flow back to the pressurized vessel after passing through the filter;

15 a secondary flow line in fluid communication with the pressurized vessel, the secondary flow line including an evaporator to evaporate a secondary flow of the pressurized fluid solvent directed through the secondary flow line into a vapor and separate contaminants therefrom;

20 a vent connected in fluid communication with the evaporator to vent the vapor from the evaporator to a location outside the system;

25 a source of pressurized fluid solvent in fluid communication with the pressurized vessel to replace pressurized fluid solvent into the pressurized vessel at a flow substantially equivalent to the secondary flow vented by the vent; and

30 a pressure equalization line in fluid communication with and extending between the source of pressurized fluid solvent and at least one of either the filter and the pressurized vessel for displacing solvent vapor therebetween.



INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/14643

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D06F43/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 D06F D06L C23G B08B D06B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE,A,39 04 514 (ÖFFENTLICHE PRÜFSTELLE UND TEXTILINSTITUT FÜR VERTRAGSFORSCHUNG E.V.) 23 August 1990 cited in the application see page 4, line 27 - line 36; claims 12-15	1-3, 9-15,32, 35,38
A	--- PATENT ABSTRACTS OF JAPAN vol. 15 no. 331 (P-1241), 22 August 1991 & JP,A,03 122598 (KOBE STEEL LTD) 24 May 1991, see abstract	16,37,43
A	--- US,A,5 316 591 (S.C. CHAO ET AL.) 31 May 1994 cited in the application see column 5, line 59 - column 6, line 9 --- -/-	1-3, 9-15,32, 35,38

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- * "A" document defining the general state of the art which is not considered to be of particular relevance
- * "E" earlier document but published on or after the international filing date
- * "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date or another citation or other special reason (as specified)
- * "O" document referring to an oral disclosure, use, exhibition or other means
- * "P" document published prior to the international filing date but later than the priority date claimed

- * "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- * "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- * "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- * "&" document member of the same patent family

Date of the actual completion of the international search

19 March 1996

Date of mailing of the international search report

01.04.1996

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

D Hulster, E

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 95/14643

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,5 339 844 (T.B. STANFORD) 23 August 1994	
A	US,A,4 513 590 (M. FINE) 30 April 1985	
A	GB,A,1 408 263 (NEIL) 1 October 1975	
A	US,A,3 542 200 (L.L. DURR) 24 November 1970	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 95/14643

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A-3904514	23-08-90	NONE	
US-A-5316591	31-05-94	CA-A- 2101142	11-02-94
		EP-A- 0583653	23-02-94
		JP-A- 6254520	13-09-94
		US-A- 5339844	23-08-94
		US-A- 5456759	10-10-95
US-A-5339844	23-08-94	US-A- 5316591	31-05-94
		EP-A- 0641611	08-03-95
		JP-A- 7171527	11-07-95
		CA-A- 2101142	11-02-94
		EP-A- 0583653	23-02-94
		JP-A- 6254520	13-09-94
		US-A- 5456759	10-10-95
US-A-4513590	30-04-85	NONE	
GB-A-1408263	01-10-75	NONE	
US-A-3542200	24-11-70	NONE	